

**REPORT ON AIR SAMPLING NEAR THE WORLD TRADE CENTER SITE
NEW YORK STATE DEPARTMENT OF HEALTH
OCTOBER 30 & 31, 2001**

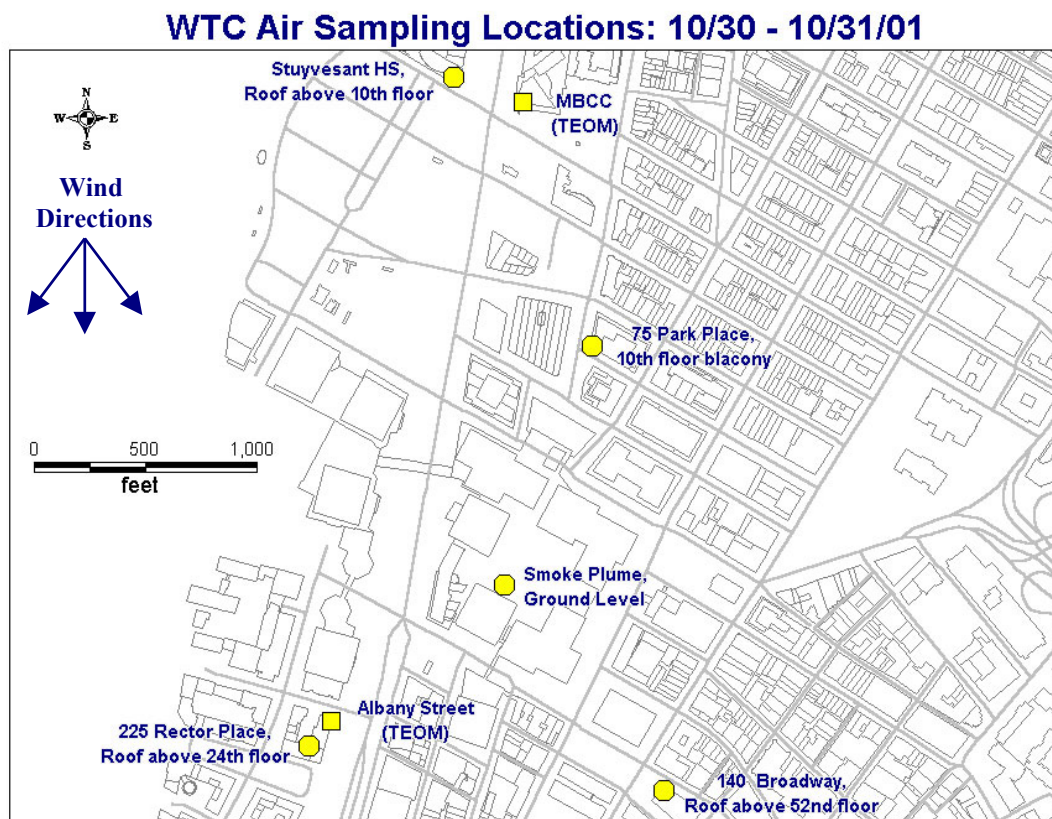
Introduction

Outdoor air was sampled on October 30 and 31, 2001, by the New York State Department of Health (NYSDOH), with assistance from the New York City Department of Health (NYCDOH), to characterize chemical and particulate releases from the smoldering debris and cleanup activities at the World Trade Center (WTC) site. Sampling occurred at four locations, two north of the site, and one each southeast and southwest of the site. Air samples were collected for a wide range of compounds, including acid aerosols, aldehydes, inorganic acids, total suspended particulate matter, and volatile organic compounds (VOCs).

Methods

Figure 1 shows the locations of sampling. Three of the locations, as well as the smoke plume from the debris pile, were previously sampled for VOCs on September 28, 2001¹. The fourth location, Stuyvesant High School, was added for this second round of sampling.

Figure 1.



Building use and occupancy differed among the locations. At the time of our sampling, 75 Park Place was an unoccupied office building, while 140 Broadway (office building), 225 Rector Place (residential building), and Stuyvesant High School were occupied. At each of these locations, samples were collected from a building roof and on the street adjacent to the building.

Light winds during sampling varied from the north to northeast on October 30 and from the northwest to north on October 31. In general, Stuyvesant HS and Park Place were upwind of the WTC site, Rector Place was downwind, and Broadway was crosswind of the site.

During sampling, the smoke plume was visibly affecting Rector Place, while not visibly affecting the other locations. Odors from the WTC site were evident intermittently at all sampling locations on both days, but they were stronger and more persistent at Rector Place.

Description of Sampling Methods

Table 1 gives the collection and analysis methods used during the October 30-31, 2001 sampling event, as well as the respective compounds of interest for those methods.

Table 1. Methods Used in the Collection and Analysis of Outdoor Air Samples

Method	Analyte	Sample Collection	Sample Duration	Locations	Analysis	Detection Limit
EPA TO-14	acrylates ketones phenolics volatile organic compounds	Summa canister	~2 hrs	roof, street, source	GC/MS	2-4 $\mu\text{g}/\text{m}^3$
light scatter	total suspended particulate	real-time	~14 - 18 hrs	roof only	DataRam	0.4 μm
NIOSH 7903	inorganic acids	sorbent tube	~2 hrs	roof, street	IC	10 $\mu\text{g}/\text{m}^3$
EPA IO-4.2	inorganic acids	denuder/filter	<1 - 13 hrs	roof, source	IC	1-2 $\mu\text{g}/\text{m}^3$
EPA TO-11	aldehydes/acetone	DNPH cartridge	~2 hrs	roof, street	HPLC	1 $\mu\text{g}/\text{m}^3$

GC/MS: gas chromatography/mass spectroscopy

DNPH: 2,4-dinitrophenylhydrazine-silica coated cartridge

HPLC: high pressure liquid chromatography

IC: ion chromatography

Air samples for volatile organic compound (VOC) analysis were collected according to the U.S. Environmental Protection Agency Method TO-14, using SUMMA[®] Passivated Canisters. Samples were collected from the roof and street at the four building locations on October 30 and 31, giving four samples from each site. Two samples were taken in the smoke plume on the debris pile on October 31. Samples at the building locations were collected over two hours, while the samples at the debris pile were collected for thirty minutes.

Real-time measurement of total suspended particulate (TSP) occurred using DataRam instruments on the roof at each of the four locations. Data were collected from the evening of October 30 through the morning of October 31. The DataRam can measure the light scattered by particles with an aerodynamic diameter between 0.4 – 100 micrometers (μm), and converts this measurement into a mass per cubic meter. The instrument was configured to read this size range. Mean TSP values were calculated at one-minute intervals to give the total mass of particles in this size range.

Two methods were used for collecting and analyzing acids, NIOSH 7903 and EPA IO-4.2. Both methods use ion chromatography, but means of collection and target analytes differ. The NIOSH method collects a sample by pulling air through a silica gel sorbent tube, trapping selected analytes. The concentrations of six acids measured were: hydrobromic acid (HBr), hydrochloric acid (HCl), hydrofluoric acid (HF), nitric acid (HNO_3), phosphoric acid (H_3PO_4), and sulfuric acid (H_2SO_4). The working range for NIOSH 7903 is 10-5000 $\mu\text{g}/\text{m}^3$. Samples were collected in duplicate at all building locations.

EPA Method IO-4.2 was also used for the collection of gas species. With this method, a sample is collected by pulling air through a $\text{PM}_{2.5}$ cutoff head, then through denuders (tubes containing etched glass cylinders) to a filter. (A $\text{PM}_{2.5}$ cutoff head restricts the size of particles passing into the system to those with an aerodynamic diameter of 2.5 μm or less.) Gases are trapped on a coating used in the denuder, and aerosols are trapped on the filter. This method was used to characterize five gas species, along with pH and particulate sulfate. The five gas species were: hydrochloric acid (HCl), nitrous acid (HNO_2), nitric acid (HNO_3), ammonia (NH_3), and sulfur dioxide (SO_2). Equipment for this sampling was deployed on rooftops at Park Place, Rector Place, and Stuyvesant HS, and later modified for use at the debris pile. Sampling times and volumes varied.

Air samples for acetone and aldehyde analysis were collected according to EPA Method TO-11, using DNPH-silica cartridges and HPLC/UV analysis. Samples were collected over a two-hour period from the roof and street at the four building locations on October 30 and 31, giving four samples from each site. No samples were obtained from the smoke plume on the debris pile due to logistical and safety reasons.

Table 2 shows the sampling times for each method, as well as the number of samples collected for each method. Evening sampling occurred from about 6:00 pm - 10:00 pm on October 30, and morning sampling occurred from about 7:00 am - 11:00 am on October 31. Both the evening and morning sampling events were at street- and roof-level. At three locations, some samples were collected overnight, beginning after the evening sampling (about 10:00 pm) and ending before the morning sampling (about 7:00 am). Sampling for acid aerosols and VOCs occurred in a smoke plume on the debris pile at the WTC site on the afternoon of October 31 from 2:00 – 2:30 pm.

Table 2. Times of Outdoor Air Sample Collection
(number of samples collected in parentheses)

Method	Broadway	Park Place	Rector Place	Stuyvesant HS	Debris Pile
EPA TO-14	evening (2) morning (2)	evening (2) morning (2)	evening (2) morning (2)	evening (2) morning (2)	afternoon (2)
EPA TO-11	evening (2) morning (2)	evening (2) morning (2)	evening (2) morning (2)	evening (2) morning (2)	not collected
EPA IO-4.2	not collected	evening (1) overnight (1) morning (1)	evening (1) overnight (1) morning (1)	evening (1) overnight (1) morning (1)	afternoon (1)
NIOSH 7903	evening (2) morning (2)	evening (2) morning (2)	evening (2) morning (2)	evening (2) morning (2)	not collected
DataRam	evening through morning (continous)	evening through morning (continous)	evening through morning (continous)	evening through morning (continous)	not collected

Air Sampling Results

Volatile Organic Compounds (VOCs)

Table 3 lists ten VOCs found at the debris pile in the highest concentrations, along with the concentrations found at the other sampling locations (results for all VOC analytes are listed in Appendix). The debris pile concentration is the average of two samples, while the other site concentrations are the range of four samples. VOC concentrations for rooftop and street-level samples were similar for each location, with the only anomaly at Rector Place, where the rooftop sample had an ethyl alcohol concentration seven times that of the corresponding street-level result. In general, the type and concentrations of VOCs found in the two debris pile grab samples were similar to what was found in the debris pile grab sample collected on September 28¹.

The debris pile had the highest VOC levels of all sampling locations. Except for ethyl alcohol, levels from the debris pile were more than 10 times higher than those measured at Rector Place. Concentrations found at Rector Place were slightly higher than the other sampling locations.

Benzene levels in the debris pile samples agreed with the lower range of those reported by EPA for three debris pile grab samples taken on October 31. Levels of benzene at the other DOH sampling locations were within, or below, the middle half of EPA's published outdoor background range².

Table 3. Range of VOC concentrations ($\mu\text{g}/\text{m}^3$) for selected analytes

Analyte	Debris Pile	Rector Place	Park Place	Broadway	Stuyvesant HS	EPA ¹	DOH ²
toluene	395	4.4 - 13.0	3.5 - 9.7	2.0 - 7.0	2.4 - 4.5	0.6 - 20	1 - 6.1
ethylbenzene	375	<2.0 - 6.8	ND - <2.0	<2.0	ND - <2.0	1 - 5.4	<1 - <6
benzene	325	2.4 - 8.2	<2.0 - 2.1	<2.0	<2.0	2 - 11	<1.6 - 4.7
isopropylbenzene	325	<2.0 - 2.9	ND	ND	ND	0	<10
acetone	240	3.5 - 6.0	2.4 - 5.2	2.4 - 9.5	<2.0 - 2.5	ND - 6.7	NA
styrene	115	ND - <2.0	ND	ND	ND	0 - 1.4	<1 - <10
methyl ethyl ketone	108	<2.0 - 2.6	ND - <2.0	ND - 2.6	ND	NA	NA
ethyl alcohol	53	12.0 - 82.0	11.0 - 16.0	9.2 - 12.0	5.0 - 10.0	NA	NA
m,p-xylene	44	<2.0	<2.0	ND - <2.0	ND - <2.0	NA	<1 - <10
chloromethane	41	<2.0 - 2.3	<2.0	<2.0	<2.0	1.3 - 1.5	<1 - 1.4

¹ Background ranges (25th – 75th percentiles) from the US EPA Volatile Organic Compounds Database, published in 1988.

² Background ranges (25th – 75th percentiles) from the NYS DOH Database for air samples collected and analyzed from 1989 through 1996.

Samples at the Debris Pile were collected for thirty minutes; samples at the other locations were collected for two hours.

ND: not detected

NA: not available

For the debris pile, twenty of the sixty-nine VOC analytes were not detected in the October samples. These same twenty were also not found in the September sample collected by NYSDOH. Six VOCs were detected in October that were not detected in September. These compounds were 1,2-, 1,3-, and 1,4-dichlorobenzene, ethylcyclohexane, tetrachloroethene, and trichloroethene. These six compounds were found at concentrations below $10 \mu\text{g}/\text{m}^3$.

High levels of trichlorofluoromethane (a refrigerant, R-11) were found in the roof samples from 140 Broadway. These findings mirror those from the September 28 sampling. The samples were taken on a parapet approximately 15 feet from an exhaust vent. As with the September 28 sampling, it is suspected that the source was a refrigerant leak from a chiller located on the 52nd floor.

We expanded the VOC analysis in the debris pile and Rector Place samples to include more compounds that are suspected to come from fires or are irritants. The compounds found in this supplemental analysis are commonly referred to as tentatively identified compounds (TICs)³. Although tentatively identified, the laboratory reported that there is a high probability the identifications are correct. However, without having the specific standards for these TICs, some uncertainty remains about their identity. These compounds are not specific to EPA Method TO-14, and without the standards, the reported TIC-VOCs concentrations can only be estimated. The TIC-VOCs included methylstyrene, acetophenone, naphthalene, and phenol (see Table 4 for the results from the debris pile). Some of the TIC-VOCs found in the debris pile samples were also found in the samples from Rector Place, but the levels were too low to even estimate a quantity. The TIC-VOC analysis was not conducted for the samples from the other locations.

Table 4. Estimated Concentrations of Tentatively Identified Compounds in Debris Pile Samples ($\mu\text{g}/\text{m}^3$)

Compound Name (TIC)	Sample 1	Sample 2
acetophenone	68.7	122.6
benzaldehyde	14.7	30.8
benzofuran	17.4	28.4
benzonitrile	46.3	88.4
biphenyl	11.3	18.3
cyclopentanone	30.2	54.9
furfural	4.3	9.0
methyl pyrrole	5.0	8.9
2-methylfuran	46.9	80.4
1-methylnaphthalene	12.2	18.0
2-methylnaphthalene	12.8	18.6
2-methylphenol	25.6	41.9
a-methylstyrene	57.9	101.3
naphthalene	62.8	94.2
phenol	161.3	261.2
thiophene	3.8	6.2

(Compounds looked for, but not found, in the supplemental analysis for the debris pile samples were acrolein, benzyl nitrile, dimethylpyrrole, nitrophenol, phthalic anhydride, and pyrazole. Chlorophenol was identified in debris pile samples, but could not be quantified.)

Particulate Measurements

Results from the particulate measurements are summarized in Table 5a. DataRam instruments were deployed on rooftops at four locations. As noted earlier, the DataRam was configured to detect total suspended particulate (TSP), or particles with a aerodynamic diameter between 0.4 – 100 μm . Data were collected from the evening of October 30 through the morning of October 31. The mean TSP at Rector Place was two to four times that measured at Stuyvesant HS and Park Place, and five to ten times the mean concentration measured at Broadway.

Table 5a. Summary of Total Suspended Particulate (TSP)

DataRam Location	October 30, 2001		October 31, 2001	
	Mean ($\mu\text{g}/\text{m}^3$)	Range	Mean ($\mu\text{g}/\text{m}^3$)	Range
Broadway	4.7	2.2 – 15.2	6.2	2.0 – 19.3
Park Place	13.3	5.9 – 44.0	14.2	5.8 – 45.8
Stuyvesant HS	13.4	7.0 – 33.3	14.4	8.5 – 40.1
Rector Place	27.7	4.9 – 125.5	65.5	7.2 – 585.7

TSP measurement times (in military hours): Stuyvesant, 16:17-10:45; Park Place, 18:18-11:11; Rector, 19:00-10:30; and Broadway, 19:44-09:45 hrs.

DataRam mean concentrations are the average of one-minute measurements of particles in the size range 0.4 – 100 μm . The range given is for all one-minute measurements.

The NYS Department of Environmental Conservation has fixed-site TEOM Series 1400a PM Monitors deployed at numerous locations in Manhattan, including Manhattan Borough Community College (MBCC, near Stuyvesant HS) and Albany Street (near Rector Place; see Figure 1). While the DataRam employs light-scattering technology, the TEOM is a filter-based real-time mass monitor for measuring particulate

concentration in ambient air. (For these samples, the TEOM measured particulates with diameters of 2.5 micrometers or less, or PM_{2.5}.)

Table 5b summarizes the data from two NYS DEC PM_{2.5} monitoring locations for the corresponding time period as that of the DataRam TSP measurements.

Table 5b. PM_{2.5} Data from Nearby NYS DEC Monitoring Locations

TEOM Location	Mean PM _{2.5} (µg/m ³)	Hourly Range	Mean PM _{2.5} (µg/m ³)	Hourly Range
Albany St	17.8	15.1 – 19.6	31.7	12.0 – 61.8
MBCC	12.8	9.4 – 15.5	9.4	5.4 – 18.6

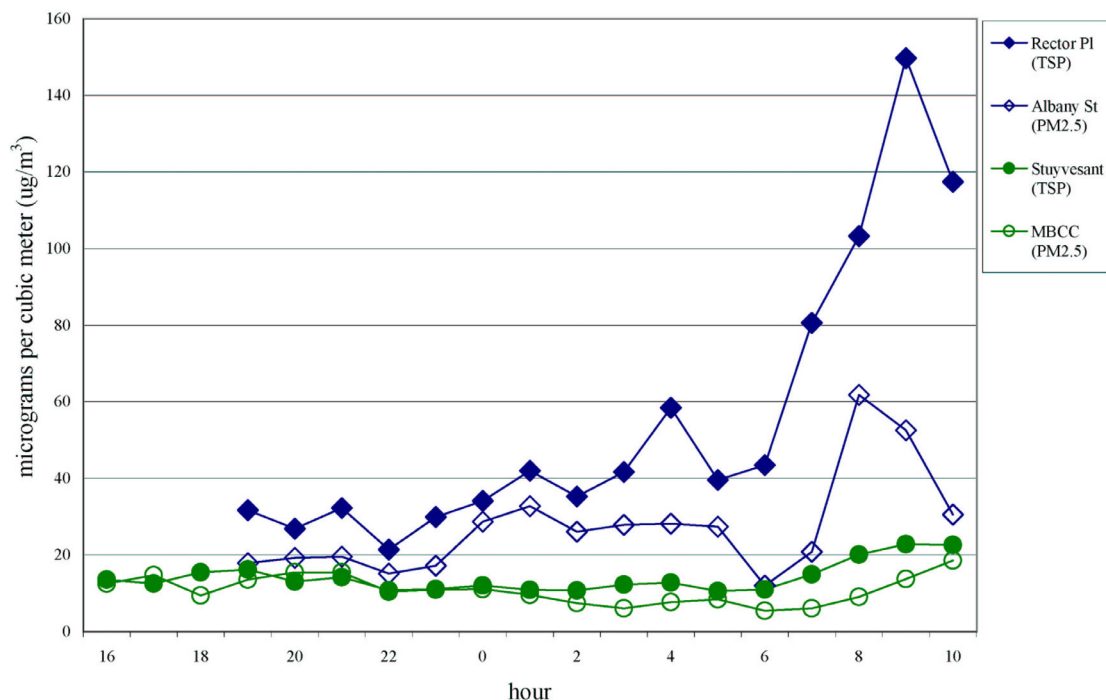
NYS DEC: New York State Department of Environmental Conservation.

Albany St and MBCC TEOM mean concentrations are one-hour averages of ten-minute measurements of particles in the size range

below 2.5 µm. The range given is for all hourly averages corresponding to the TSP sampling period.

DataRam TSP results were compared with the TEOM data from the DEC sites for the length of the sampling period. Figure 2 shows the DEC PM_{2.5} data from Albany Street and MBCC with the TSP data collected at Rector Place and Stuyvesant HS. (One-hour averages were calculated for the TSP data to correspond with the TEOM data by averaging 60 one-minute measurements.)

Figure 2. DataRam vs. TEOM, October 30 and 31, 2001



The DataRam measures particulates with a diameter of 0.4 – 100 µm (TSP). The TEOM measures particulates with a diameter of 2.5 µm or less (PM_{2.5}). TSP data includes PM_{2.5}, PM₁₀, and all particulate sizes up to PM₁₀₀.

The two upwind locations, Stuyvesant HS and MBCC, track each other well, as do the two downwind locations, Rector Place and Albany, especially considering that each method measures a different particulate size range using different time intervals.

The sampling site at Rector Place was affected by the plume from the debris pile for the majority of the sampling period, especially on the morning of October 31. Staff at this location detected strong odors and smoke from the debris pile, and also witnessed dust gathering on the instruments. No smoke or dust was observed at the other sampling locations. The TSP levels were the highest at Rector Place, and spiked on the morning of October 31. A corresponding spike was also seen in the PM_{2.5} data from Albany Street (see Figure 2). TSP levels at Rector Place ranged from one to three times the PM_{2.5} levels found at Albany Street.

Broadway's crosswind location, as well the sampler's position on the roof of the 52-story building may have both played a role in the lower levels of TSP measured. Broadway was the tallest building on which samples were collected. Larger particulates tend to settle, and the lower values for TSP seen at the Broadway site may have been related to the building's height.

Acid Aerosols and Gases

NIOSH Method 7903 was used for the collection of six acids: hydrobromic, hydrochloric, hydrofluoric, nitric, phosphoric, and sulfuric acids (HBr, HCl, HF, HNO₃, H₃PO₄, and H₂SO₄, respectively). Samples were collected in duplicate over a 2-3 hour period at roof and street level. Table 6 provides concentration ranges for four of the six acids tested. Neither hydrobromic nor nitric acid was found in any of the samples, so they are not included in the table. (See Appendix 2 for individual sorbent tube results.)

Hydrofluoric acid was detected at all sampling sites, regardless of wind direction on October 30 and 31. Sulfuric acid was found at or above 10 µg/m³ in all eight samples collected at Rector Place. No samples at Broadway, Park Place, or Stuyvesant HS exceeded 10 µg/m³ for either phosphoric or sulfuric acid. Phosphoric acid was detected in only one sample (10/31 Rector Place roof sample). Rector Place was the only location at which hydrochloric, phosphoric, and sulfuric acid were all found using the NIOSH method. Similarly, except for hydrofluoric acid, the levels found at Rector Place were higher. These results suggest that the WTC plume may have contained hydrochloric, phosphoric, and sulfuric acids. However, these data are limited and the reported concentrations are near the lower working range of the method, increasing the uncertainty in the sample analysis.

Table 6. Range of Inorganic Acid Concentrations ($\mu\text{g}/\text{m}^3$)

Date	Site	HF	H ₂ SO ₄	H ₃ PO ₄	HCl
10/30/01	Broadway	<10 – 20	<10 – 10	<10	<10
	Park Place	11 – 14	<10	<10	<10 – 10
	Rector Place	<10 – 15	12 – 19	<10	<10
	Stuyvesant HS	<10	<10	<10	<10
10/31/01	Broadway	<10 – 11	<10	<10	<10
	Park Place	19 – 21	<10	<10	<10
	Rector Place	<10 – 13	10 – 14	<10 – 16	11 – 15
	Stuyvesant HS	10 – 17	<10	<10	<10

The NIOSH Method 7903 working range is 10 – 5000 $\mu\text{g}/\text{m}^3$. “<10” means the sample was below 10 $\mu\text{g}/\text{m}^3$. The October 31 samples from the roof at Park Place could not be analyzed due to the inadequate air volume sampled.

HCl: hydrochloric acid

H₂SO₄: sulfuric acid

HF: hydrofluoric acid

H₃PO₄: phosphoric acid

Tables 7 and 8 summarize the data from EPA Method IO 4.2, which involves the use of an annular denuder system. It was used to characterize five gas species, along with pH and PM_{2.5} particulate sulfate. The five gas species were: hydrochloric acid, nitrous acid, nitric acid, ammonia, and sulfur dioxide (HCl, HNO₂, HNO₃, NH₃, and SO₂, respectively).

This system was previously used in Manhattan as part of a long-term monitoring effort focused on potential irritants linked to asthma⁴. Data for pH and particulate sulfate were collected from January 1999- November 2000. Annular denuder extract data were collected from July 1999- June 2000. Results from that monitoring are included in Tables 7 and 8. Note that the results provided for 1999 and 2000 are from 24-hour, 14400-liter air samples. Volumes from the WTC sampling vary due to field conditions (e.g., an area in which to sample the debris pile could only be secured for thirty minutes). Still, the historical conditions in Manhattan can provide a reference with which to view the October 30-31 results.

As shown in Table 7, the debris pile sample had the highest level of particulate sulfate, as well as the lowest pH of any samples collected. In general, particulate sulfate levels were higher at Rector Place than at Park Place or Stuyvesant HS, especially on the morning of October 31. As discussed in the previous section (Particulate Measurements), staff experienced odors and smoke at Rector Place, most strongly on October 31. Levels of pH were similar at the three locations sampled, and were slightly higher than what had been seen previously in Manhattan during 1999 and 2000.

Table 7. Annular Denuder System Filter Results

Date	Sample	Time (min)	Vol (L)	Site	pH	Particulate Sulfate ¹ (µg/m ³)
10/30/01	PM	173	1730	Park Place	5.69	1.6
10/30-31/01	PM-AM	749	10415	Park Place	5.74	0.7
10/31/01	AM	139	1254	Park Place	5.57	2.6
10/30/01	PM	186	1860	Rector Place	5.54	1.3
10/30-31/01	PM-AM	517	5170	Rector Place	5.58	5.6
10/31/01	AM	181	1810	Rector Place	5.80	8.2
10/30/01	PM	294	2940	Stuyvesant HS	5.81	2.0
10/30-31/01	PM-AM	534	8544	Stuyvesant HS	5.69	0.5
10/31/01	AM	247	3952	Stuyvesant HS	5.58	0.8
10/31/01	PM	30	510	Debris Pile	4.71	56.5
Extreme value for October-November 1999 and 2000 ²					4.37	12.2
Mean for October-November 1999 and 2000 ³					5.11	3.3
Extreme value for Study Period ⁴					3.54	23.9
Mean for Study Period ⁵					5.04	4.0

PM-AM: These samples were collected overnight.

Note: (2) – (5) represent results from sampling done near 2nd Ave. and 14th St. in Manhattan during 1999 and 2000. These results are from 24-hour samples.

¹ An elutriator-accelerator head was used to select particulate matter with a diameter of 2.5 micrometers or less.

² These values represent the lowest pH (“most acidic”) and highest particulate sulfate concentration measured from October through November of 1999 and 2000.

³ Average pH and particulate sulfate concentration measured from October through November of 1999 and 2000.

⁴ These values represent the lowest pH and highest particulate sulfate concentration measured from January 1999 through November 2000 (“the Study Period”).

⁵ Average pH and particulate sulfate concentration measured from January 1999 through November 2000.

The elevated levels of particulate sulfate levels seen at Rector Place suggest an influence from the WTC site. The lower pH found in the aerosol sample from the debris pile compared to the pH of the aerosol samples from Rector Place suggests that the aerosol acidity is being neutralized by a base, possibly gaseous ammonia (which was found at elevated levels at the debris pile). This is consistent with the decrease in levels of sulfuric acid gas, particulate sulfate, and ammonia gas found in the Rector Place samples compared to the debris pile. Although particulate sulfate levels were higher at Rector Place than the other off-site sampling locations, they were within the range of what was found in Manhattan during October and November of 1999 and 2000.

As shown in Table 8, hydrochloric acid concentrations ranged from 0.08-1.38 µg/m³ (excluding the debris pile). From October through November 1999, the maximum daily concentration of HCl was 0.68 µg/m³. Five samples from the October 30-31 sampling exceed that concentration. However, only the debris pile sample exceeds the highest daily value measured in the study (July 1999, 2.95 µg/m³).

Levels for nitrous acid, even at the debris pile, were below the maximum daily concentration measured during October-November 1999 ($10.4 \mu\text{g}/\text{m}^3$).

Three samples exceeded the October-November 1999 daily maximum of nitric acid ($1.84 \mu\text{g}/\text{m}^3$), but none, including the debris pile sample, exceeded the July 1999 maximum daily value of $14.66 \mu\text{g}/\text{m}^3$.

For ammonia, five of the October 30-31 samples exceeded the daily maximum in the study (May 2000 $10.80 \mu\text{g}/\text{m}^3$). The debris pile sample was over sixty-six times the May 2000 daily maximum value.

The mean October-November 1999 sulfur dioxide concentration of $25.4 \mu\text{g}/\text{m}^3$ was exceeded by six of the samples, but none, including the debris pile sample, exceeded the highest daily maximum seen in November 1999 of $67.7 \mu\text{g}/\text{m}^3$.

Table 8. Annular Denuder Extracts ($\mu\text{g}/\text{m}^3$)

Date	Sample	Time (min)	Vol (L)	Site	HCl	HNO ₂	HNO ₃	NH ₃	SO ₂
10/30/01	PM	173	1730	Park Place	0.88	ND	1.79	5.69	13.06
10/30-31/01	PM-AM	749	10415	Park Place	0.11	ND	0.29	3.30	16.37
10/31/01	AM	139	1254	Park Place	1.23	1.33	3.66	15.98	50.18
10/30/01	PM	186	1860	Rector Place	0.19	1.24	1.15	20.32	46.68
10/30-31/01	PM-AM	517	5170	Rector Place	0.90	0.16	1.12	27.34	29.85
10/31/01	AM	181	1810	Rector Place	1.38	0.80	2.19	41.32	47.12
10/30/01	PM	294	2940	Stuyvesant HS	0.61	0.39	0.85	4.89	10.10
10/30-31/01	PM-AM	534	8544	Stuyvesant HS	0.08	0.10	0.30	3.63	16.00
10/31/01	AM	247	3952	Stuyvesant HS	0.19	0.49	1.00	5.60	26.15
10/31/01	PM	30	510	Debris Pile	33.90	2.24	12.28	715.1	58.70
Max for October-November 1999 ¹					0.68	10.40	1.84	NA	67.7
Mean for October-November 1999 ²					0.26	4.51	0.51	NA	25.45
Max for Study Period ³					2.95	16.84	14.66	10.80	156.8
Mean for Study Period ⁴					0.51	3.21	1.75	3.54	26.36

PM-AM: These samples were collected overnight.

NA: not available

See Appendix 3 for complete annular denuder results.

Note: (1) – (4) represent results from sampling done near 2nd Ave. and 14th St. in Manhattan during 1999 and 2000. These results are from 24-hour samples.

¹ These values represent the highest concentrations measured from October through November of 1999.

² Average concentrations measured from October through November of 1999.

³ These values represent the highest concentration measured from July 1999 through June 2000.

⁴ Average concentrations measured from July 1999 through June 2000.

For the three locations sampled outside of the WTC site, higher levels were seen for almost all compounds on the morning of October 31. Nitric acid, nitrous acid and sulfur dioxide were all higher at Park Place than at Rector Place on the morning of October 31. This does not follow the expected pattern (seen with total suspended particulate) that Rector Place, being downwind of the WTC site, should have been the location where higher concentrations are found. Although apparently upwind, Park Place's proximity to the WTC site, as well as canyon effects from nearby buildings on the

wind, may have resulted in some influence from the WTC site smoke plume. However, given that many of the other contaminants monitored did not show this increase, it is more likely these elevated levels may have been due to a local source that may or may not have been related to the WTC.

The collection time for the sample from the debris pile was much shorter than for the other locations. Concentrations of chemicals in ambient air can fluctuate substantially over short time intervals. Transient spikes in concentration can be seen or completely missed in short-term grab samples. The shorter sample collection time at the debris pile may partially explain the large concentration differences seen between the pile and the other locations, as well as from the long-term study done in 1999 and 2000.

Acetone and Aldehydes

EPA Method TO-11 was used for the collection and analysis of air samples for acetone and aldehyde analysis. Samples were collected over a two-hour period from the roof and street at the four off-site sampling locations, giving four samples per site. Table 9 summarizes the results. (See Appendix 4 for the complete results.) Concentrations are the range of four samples, except at Rector Place, where one sample was lost due to pump failure.

(This method for the collection and analysis of aldehydes was used in Manhattan as part of a long-term monitoring effort focused on potential air contaminants linked to asthma. Note that these samples were collected over a twenty-four-hour period, while the samples around the WTC site were collected over a two-hour period. Aldehyde data for this study was collected daily from January 1999 to November 2000². Results from that monitoring can provide a framework in which to view the October 30-31, 2001 sampling.)

Table 9. Summary of Aldehyde Results
Range of Concentrations from All Samples Collected ($\mu\text{g}/\text{m}^3$)

Analyte	Broadway	Park Place	Rector Place	Stuyvesant HS	Oct-Nov '99-'00 ¹	Study Period ²
formaldehyde	1.7 - 6.6	2.8 - 13.5	1.5 - 9.2	1.8 - 6.0	1.4 - 8.9	<1.0 - 15.4
acetaldehyde	1.0 - 19.7	3.1 - 14.4	2.1 - 5.9	1.4 - 1.7	1.0 - 7.1	<1.0 - 13.6
acetone	<1 - 35.6	12.4 - 20.5	17.3 - 26.5	7.6 - 11.9	2.1 - 21.2	<1.0 - 40.4

Note: Only three samples from Rector were used to calculate the average; the 10/30/01 roof sample was lost due to pump failure. See Appendix 4 for all analyte and sample results.

(1) and (2) represent results from sampling done near 2nd Ave. and 14th St. in Manhattan during 1999 and 2000. These results are from 24-hour samples.

¹ These values represent the range of daily (24 hr) average concentrations measured from October through November 1999 and 2000.

² These values represent the range of daily (24 hr) average concentrations measured from January 1999 through November 2000 (the "Study Period").

Only three of the fifteen analytes were detected: acetaldehyde, acetone, and formaldehyde. The Park Place sampling location had the highest formaldehyde concentration, while Broadway had the highest acetaldehyde concentrations. Levels of acetone were similar at Broadway, Park Place, and Rector Place, as were levels of

formaldehyde at Broadway, Rector Place, and Stuyvesant HS. Concentrations for rooftop and street-level samples were similar at each location. The concentrations for the aldehydes detected are generally within the range of values seen in Manhattan between January 1999 and November of 2000. Given that samples from locations upwind, crosswind, and downwind of the smoke plume had similar results, it appears that these contaminants were not influenced by the WTC site.

For the Oct-Nov 1999 and 2000 samples, the highest daily maximum concentration of formaldehyde was $8.9 \mu\text{g}/\text{m}^3$. One sample at Park Place and two samples at Rector Place met or exceeded this concentration, but none exceeded the highest daily maximum measured during the study period (July 1999; $15.4 \mu\text{g}/\text{m}^3$). Three samples (one at Broadway, two at Rector Place) exceeded the October-November 1999-2000 daily max for acetone ($21.2 \mu\text{g}/\text{m}^3$), but none exceeded the study's highest daily max (August 1999; $40.4 \mu\text{g}/\text{m}^3$). For acetaldehyde, three samples (one at Broadway, two at Park Place) exceeded the highest daily max for both October-November 1999-2000 ($7.1 \mu\text{g}/\text{m}^3$) and the study (August 1999; $13.6 \mu\text{g}/\text{m}^3$). As with the acid data, the shorter collection time of the October 30-31, 2001 samples may have contributed to the concentration differences seen in these samples as compared to the long-term study data.

Public Health Implications

The highest levels of chemicals were found in samples taken from the plume at the World Trade Center debris pile. Several chemicals directly from the plume exceeded both typical background levels and air comparison values. However, these results are unlikely to represent the potential exposure of the residents, since residents were unlikely to have been directly in the plume at the debris pile for any length of time. Sampling results at areas potentially affected by the plume but not at the debris pile are more relevant for evaluating potential exposure to the residents. In general, the levels of VOCs detected at locations away from the plume were lower in the October 30-31 sampling than in the sampling conducted on September 28¹.

Volatile Organic Compounds (VOCs)

The sampling results for 140 Broadway, 75 Park Place, and Stuyvesant High School showed that the average air levels for VOCs were generally within the ranges of typical background levels. The average levels of dichlorodifluoromethane and trichlorofluoromethane exceeded typical background levels at all three of these locations, but none of the levels of these or any other VOCs measured above background at these locations exceeded an air comparison value for cancer or noncancer health effects. Air comparison values are used as screening tools for evaluating the health significance of environmental air sampling results. The cancer comparison value is the air concentration that is estimated, on long-term exposure, to result in an increased lifetime cancer risk of one-in-one million. The noncancer air comparison value is an estimate of an air concentration that is likely to be without an appreciable risk of noncancer health effects on long-term exposure.

The 225 Rector Place location was the site most directly downwind from the WTC debris pile on the days the samples were taken. Consequently, the levels of VOCs detected at this location were generally higher than those at the other locations away from the debris pile. The average levels of benzene, chloromethane, dichlorodifluoromethane, isopropylbenzene, methyl ethyl ketone, toluene, and trichlorofluoromethane were above typical background levels. However, benzene and chloromethane were the only chemicals detected at levels that exceed both typical background levels and health comparison values. The benzene and chloromethane air concentrations (as well as typical background concentrations for these chemicals) exceed their comparison values based on carcinogenic effects following long-term exposure. We do not expect that community exposures to these levels will result in cancer risks that are appreciably increased over those resulting from exposure to background levels. The estimated duration of exposure is at most one year, and the elevated levels are unlikely to exist for extended periods of time due to wind direction changes (i.e., the Rector Place location is not always downwind from the debris pile). The estimated increased cancer risk for the average levels of benzene and chloromethane detected at the Rector Place location does not exceed one-in-ten thousand, above which actions are usually taken to reduce exposure.

The average level of benzene on the roof of 225 Rector Place slightly exceeds the air comparison value based on noncancer effects and long-term exposure. The street level sample at this location is slightly below this air comparison value. The noncancer air comparison value for benzene is set about 1000 times lower than the exposure level associated with adverse effects on the blood in mice exposed regularly for about six months. No health comparison values for short-term (e.g., less than two weeks) or intermediate (e.g., between two weeks and less than one year) exposure were exceeded at any location.

Results for Acetone and Aldehydes

The only chemicals detected in the acetone and aldehyde analysis at the four sampling locations away from the debris pile were acetaldehyde, formaldehyde, and acetone. The average air concentrations of acetaldehyde and formaldehyde did not exceed typical outdoor background air concentrations. The average air concentrations of acetone at all four sampling locations exceeded typical outdoor background air concentrations, but were well below air comparison values for short-term, intermediate, and long-term exposure.

Acid Gases

As with the VOCs, the levels of acid gases were generally higher in the downwind location (225 Rector Place). Almost none of the measured levels of acid gases exceeded available air comparison values for long-term, intermediate, or short-term exposure. The only exception to this was the lone detection of phosphoric acid at 225 Rector Place, which exceeded its air comparison value for long-term exposure. The level

of phosphoric acid detected at this location is about 200 times lower than the air concentration that is associated with lung damage in rats exposed regularly for about three months.

Total Suspended Particulate (TSP)

The average concentration of TSP at the four rooftop samplers varied somewhat with location. The sampler at Rector Place measured the highest average TSP concentrations. The Broadway monitor had the lowest average TSP, while Park Place and Stuyvesant HS had intermediate (and similar) average TSP concentrations. The average concentrations of TSP measured at the four monitoring locations indicate that the air concentration of TSP at any of the locations is unlikely to exceed the 24-hour New York State ambient air standard for TSP. This 24-hour standard is set at 240 micrograms per cubic meter, to protect against adverse respiratory effects. The TSP standard does not address shorter duration exposures to particles, or the potential for irritation from those exposures. There are occupational guidelines for particle concentration in workplace air that are based on preventing irritation from workday exposures to particles. The American Conference of Governmental and Industrial Hygienists (ACGIH) guideline for an eight-hour exposure to particles (comparable in size to those measured as TSP) in workplace air is 10 milligrams per cubic meter (or 10,000 micrograms per cubic meter), a level approximately 40 times higher than the NYS 24-hour TSP ambient-air standard. The average TSP levels measured at the four sampling locations fall well below this guideline level.

Irritant effects from short-term exposure to acid gases, VOCs, and particulates

Many of the airborne chemicals (including particulates) measured at and around the WTC site have unpleasant odors and/or can be irritating to the mucous membranes of the eyes, nose, and throat. Irritation effects may occur after brief exposures lasting only seconds or minutes and generally disappear shortly after exposure ceases. Eye and upper-respiratory irritation can be caused by exposure to substantial levels of many of the VOCs measured in the air samples (including aldehydes and acetone), as well as by inorganic acids and airborne particles (measured as TSP). Many VOCs and inorganic acids also have strong (and often unpleasant) odors that are usually detectable at much lower levels than are irritation effects. The anecdotal reports of persons near the WTC site experiencing eye, nose, or throat irritation are consistent with the presence of a complex mixture of airborne irritant gases and particles in the area surrounding the site.

It is difficult to evaluate precisely what airborne chemicals contributed to the irritation effects experienced in the area of the WTC site. The debris pile emissions are complex mixtures of many organic and inorganic gases, as well as particles. Although data are available to assess the irritant and odorant potential of many individual chemicals, evaluating the likely effect of short-term exposure to the mixture has substantial uncertainties. One reason for this is that the components of the mixture vary over time. Another is that the biological bases (i.e., the nervous-system mechanisms) of odor and irritation perception suggest that the response to chemicals in a mixture may be

different than what would be expected if the mixture components all behaved independently of each other.

An attempt was made to evaluate the VOC data (including the separate aldehyde and acetone analysis) for the odor and irritancy potency of the mixture detected in the air samples from the debris pile and surrounding locations. A worst-case screening approach was used by focusing on the highest estimated air concentration for each VOC from any of the samples collected at or in the area of the WTC site. Most maximum values were measured at the debris pile and therefore may not be representative of community exposure levels.

Individually, no VOC detected in any of the samples, including those from the debris pile, was measured at a level exceeding a short-term human nasal or eye irritation threshold, although many exceeded their individual odor thresholds. For most VOCs, nasal, throat, or eye irritation thresholds are higher than odor thresholds, often exceeding odor thresholds by factors of 10 – 1000. One limitation on assessing the irritancy of the VOCs mixtures from the WTC site is that the VOC samples were collected for about two hours, meaning that any short-term spikes in VOC levels would not be well characterized by the two-hour time-weighted average levels. Since odor and irritant effects occur with very short exposures, a dilution of short-term peak exposure levels could mask actual exposures that would be large enough to cause such effects. In order to account for this effect, a time-weighting adjustment was made to published odor and irritation thresholds such that two-hour threshold equivalents were estimated based on data for three-second thresholds. The time-weighting adjustment is based on a standard toxicological model, developed using experimental data for a number of chemicals, where acute effects are proportional to the product of exposure concentration raised to an exponent and exposure time (known as Haber's Law). Therefore, if exposure time increases, the concentration producing the same health endpoint would decrease. The greater the difference between the exposure duration for the data used in the model and the exposure duration for the estimated values, the greater the uncertainty in the predicted results. That is, a threshold level for a 2-hour exposure estimated from a threshold level for a 3-second exposure is more uncertain than estimating a threshold level for a 2-hour exposure from a threshold level for a 1-hour exposure.

A further difficulty with considering each chemical individually to evaluate complex mixtures for effects such as irritation is that chemicals may interact to yield different results collectively than would be expected based on each chemical's individual properties. There are data from a number of human studies of irritancy and odor perception showing that mixtures of chemicals can be detected by smell or by irritation when each of the individual chemical components is below their own odor or irritation threshold – referred to as perception "additivity". Additivity may be partial or complete, and chemicals may interact in other ways besides additivity when being sensed as part of a mixture. To account for possible effects of chemical interactions in mixture exposure, complete additivity was assumed for odor and irritant detection of the complex mixture of VOCs measured in the area of the WTC site. The effect of this assumption is to decrease the odor or irritation detection threshold for each individual component of a

mixture as the number of components in the mixture increases. For complete additivity, detection of the mixture can be assessed by computing the ratio of each chemical's concentration in air with that chemical's odor or irritation threshold. Detection of the mixture would occur if the sum of those ratios exceeded one. For example, in a mixture of two odorous chemicals, complete additivity would imply that the mixture would have a detectable odor if each chemical was present in air at a concentration of at least one-half the odor detection threshold level for each chemical. If no additivity occurs when exposed to a mixture in air, at least one of the mixture components would have to be present at a level at least equal to its odor or irritation threshold for the entire mixture to be detected by odor or irritancy.

The time-weighting adjustment (using Haber's Law) and the complete additivity adjustment described above were made to odor and irritation thresholds for the VOCs detected in the area of the WTC site. The results suggest that brief exposures to the mixture of chemicals emitted from the site at the highest levels found in the samples might fall just below the level that would be expected to cause nose, throat, or eye irritation. The assumptions of sample time-weighting and additivity of effect and the use of the highest measured air concentration data for each VOC are all conservative or worst-case assumptions. On the other hand, this analysis was unable to account for all of the chemicals potentially present in WTC emissions due to sampling limitations. This analysis did not consider irritancy from particulates and inorganic acids, both of which are present in the air sampled around the WTC site, and both of which are eye and respiratory irritants (see below). Additionally, many known irritants or highly odorous VOCs (such as carboxylic acids, amines, mercaptans, and isocyanates) were not analyzed due to analytical or sampling limitations. If any of these were present in the WTC emissions, they would contribute further to the collective irritant and odorant effects of exposure to the emissions, and would make it more likely that exposure to the mixture would exceed the modeled sensory irritation threshold.

This screening approach for evaluating VOC mixtures could not include data on particulates or inorganic acids because of differences in suspected odor and irritancy mechanisms between these chemicals and the VOCs. Particulates and inorganic acids are significant upper respiratory and eye irritants that were detected in many of the air samples collected in the area of the WTC site. Based on limited odor threshold data for inorganic acids and occupational guidelines for respiratory irritation effects in workers exposed to airborne particles, the measured levels generally did not exceed individual odor thresholds or irritancy guideline values. However, as noted above, the perception of odor or irritation from exposure to a mixture may be different from what individual thresholds would predict. Also, as was true for the VOC data, the relatively long sampling times used for particulates and inorganic acids may mask short-term "spikes" that could cause transient odor or irritation effects. For example, hydrogen fluoride (HF) was detected in over half of the sorbent tube samples collected, and the highest level detected was only about 2-fold lower than the HF odor threshold, suggesting it could contribute to occasional odors by itself at slightly higher peak levels.

Limitations of Sampling

Although this was a substantial sampling effort, the total number of analyses performed was small in comparison to all of the known possible chemicals resulting from fires or combustion processes. The sampling was conducted in a relatively short period of time (16 hours) and does not include an extensive number of samples. Concentrations of most chemicals and particulates in ambient air can fluctuate substantially at a location over short time intervals. Short-term grab samples or measurement are more likely to show transient spikes in concentration than are samples with longer averaging times. Longer sampling times are less influenced by spikes than shorter sampling times. Some of our sampling intervals do not necessarily correspond to the ideal sampling times for using health comparison values.

One of the analyses performed, the TIC analysis on the VOC samples, only allows us to identify the presence of a compound and estimate the concentration. The TICs we identified are present in the samples, but we cannot be certain of the concentrations, and have therefore provided estimates.

The results presented only characterize the composition of the ambient air on October 30 and 31, 2001. Although we can draw some general conclusions from the data, many variables may influence exposure, such as geographic variation, weather effects, changes in the cleanup operation, or residential movement and activity around the site. Additionally, because of logistical problems such as available equipment and electrical power, not all locations were equipped with the full range of sampling instrumentation. For example, safety concerns and logistics prevented investigation of all the analytes at the debris pile. Due to the large number of heavy vehicles operating on and around the debris pile, a safe area for sampling could only be secured for limited time.

Conclusion

The results of the monitoring suggest that the levels of some compounds at the debris pile were significantly elevated above typical background levels. The elevation above background levels for some of the compounds measured supports the hypothesis that combustion products were contributing to symptoms of eye, nose, and throat irritation that were reported in workers and residents in the WTC neighborhood. No specific gas or type of particulate was identified which may have caused the irritancy reported. However, the use of a simple mathematical model to estimate the irritant effects of exposure to chemical mixtures did indicate that some odor and irritation thresholds for VOC mixtures were likely to have been exceeded.

It is expected that the concentrations of the measured compounds decreased as the combustion of debris was brought under control and extinguished. Levels of some VOCs associated with fuel emissions from recovery and removal vehicles on the site will fluctuate during periods of high and low activity.

References

1. A copy of this report, *VOC Monitoring Near the World Trade Center Site, New York State Department of Health, September 28, 2001*, is located on the NYS DOH website. Address: <http://www.health.state.ny.us/nysdoh/alert/voc/voc.htm>.
2. The United States Environmental Protection Agency Volatile Organic Compounds Database is a compilation of indoor and outdoor data from studies across the United States, published in 1988.
3. The identification of a Tentatively Identified Compound (TIC) is based on the analyst's interpretation of the unknown spectra, comparison to the NIST98 Mass Spectral Database and determination of a retention index for the unknown. Quantitation of the TIC VOC is determined by dividing the areas of the TIC extracted ions by the internal standard and multiplying by the internal standard's concentration, which is 10ppbV. The response factor is assumed to be one (1) for all of the TICs. It should be understood that the quantitation of the TIC VOCs represents only the estimated on column weight and does not take into account the behavior of the TIC VOCs in the canister, nor the actual inlet system efficiency and GC/MS response. As a result, the estimated TIC VOC concentrations may be an under estimate of the actual concentration present at the time of sampling.
4. Bari, A., Ferraro, V., Dutkiewicz, V.A., Judd, C.D., Wilson, L.R., Luttinger, D., Husain, L. Measurements of gaseous HONO, HNO₃, SO₂, HCl, NH₃ and particulate sulfate and PM_{2.5} in New York. Submitted to *Atmospheric Environment*.

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Appendix 1.
Volatile Organic Compound (VOC) Results from Outdoor Air Samples
Collected at the World Trade Center and Surrounding Area, October 30 and 31, 2001

ANALYTE	N Tower Plume 10/31 2PM			225 Rector Place			140 Broadway			75 Park Place			Stuyvesant High School			Outdoor Background ^d	
	Street	Roof	Street	Street	Roof	Street	Street	Roof	Street	Street	Roof	Street	Street	Roof	Street	Roof	Roof
	10/30	10/30	10/31	10/30	10/31	10/30	10/30G	10/30	10/31	10/30	10/30	10/30	10/30	10/30	10/30	10/31	10/31
DICHLORODIFLUOROMETHANE	8.6	12	12	3.8	5.3	3.9	4.9	4.9	10/31	3.2	11	3.7	6.9	5.0	3.1	L120	10/31
1,2-DICHLOROTETRAFLUOROETHANE	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
CHLOROMETHANE	24	58	24	L120	L120	2.2	2.3	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
VINYL CHLORIDE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
BROMOMETHANE	3.6	6.8	3.6	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CHLOROETHANE	L120	4.5	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ETHYL ALCOHOL	36	71	12	82	14	19	3.2	3.1	2.5	9.2	12	11	9.4	15	5.0	9.8	10
TRICHLOROFLUOROMETHANE	3.5	5.7	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,1,2-TRICHLOROETHYLENE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ACETONE	170	310	3.5	5.4	6.0	5.5	2.4	6.0	6.0	9.5	2.4	2.4	2.7	4.3	2.5	2.3	2.3
1,1-DICHLOROETHYLENE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
METHYLENE CHLORIDE	3.0	6.5	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
METHYL-tert-BUTYL ETHER	10	16	L120	L120	L120	3.4	2.9	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
n-HEXANE	23	45	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,1-DICHLOROETHANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
2,4-DIMETHYLPENTANE	3.0	5.8	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
METHYL ETHYL KETONE	77	140	L120	L120	L120	2.6	2.3	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CIS-1,2-DICHLOROETHYLENE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CHLOROFORM	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
2,4-DIMETHYLPENTANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
TRICHLOROETHYLENE	26	51	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CYCLOHEXANE	76	15	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,1,1-TRICHLOROETHANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ISOOCTANE	2.7	4.9	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CARBON TETRACHLORIDE	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
n-HEPTANE	22	38	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,2-DICHLOROETHANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
BENZENE	260	390	2.4	4.1	8.2	8.1	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
TRICHLOROETHYLENE	L120	2.1	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
METHYLCYCLOHEXANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,2-DICHLOROPROPANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
METHYLMETHACRYLATE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
METHYL ISOBUTYL KETONE	4.4	9.5	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CIS-1,3-DICHLOROPROPENE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
n-OCTANE	L12	23	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
TOLUENE	330	460	4.4	7.2	13	13	2.0	7.0	6.0	4.4	4.2	3.5	9.7	8.2	2.4	3.2	4.5
TRANS-1,3-DICHLOROPROPENE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ETHYLMETHACRYLATE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CYCLOHEPTANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,2,3-TRICHLOROETHANE	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ETHYLCYCLOHEXANE	4.5	7.7	L130	L130	L130	3.3	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
1,2-DIBROMOETHANE	4.4	6.7	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
n-NONANE	16	27	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
CHLOROBENZENE	11	20	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ETHYLBENZENE	310	440	L120	3.2	6.8	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
m-XYLENE	36	53	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
p-XYLENE	52	49	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
STYRENE	80	150	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ALPHA-PINENE	L120	2.9	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
ISOPROPYLBENZENE	270	380	L120	L120	L120	2.7	2.9	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,1,2,2-TETRACHLOROETHANE	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
n-DECANE	12	22	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
n-PROPYLBENZENE	21	34	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,3,5-TRIMETHYLBENZENE	22	36	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
tert-BUTYLBENZENE	L120	2.2	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
sec-BUTYLBENZENE	16	24	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,2,4-TRIMETHYLBENZENE	3.8	6.4	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
d-LIMONENE	L120	2.3	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,3-DICHLOROBENZENE	L130	4.4	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
1,2,3-TRIMETHYLBENZENE	6.4	9.8	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,4-DICHLOROBENZENE	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
n-UNDECANE	12	19	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
n-BUTYLBENZENE	6.7	11	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,2-DICHLOROBENZENE	5.2	7.5	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
n-DODECANE	13	22	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120	L120
1,2,4-TRICHLOROBENZENE	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130	L130
HEXACHLORO-1,3,5-TRIAZINE	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140	L140

Samples were collected by Summa canisters (EPA Method TO-14) for a 2-hour period; the plume samples were 30 minute grabs. Samples were analyzed by the Wadsworth Center, NYS DOH.

The US Environmental Protection Agency Volatile Organic Compounds Database (EPA) is a compilation of indoor and outdoor data from studies across the United States, published in 1988.

The NYS Department of Health Database (NYSDOH) is a summary of indoor and outdoor air sample results in control homes collected and analyzed by the NYSDOH from 1989 through 1996.

The means are the 25th - 75th percentile (middle half) of the data from the EPA and NYSDOH databases.

"L1" means less than, the number following this symbol (L1) is the lowest level the laboratory test can reliably measure (detection limit).

If there is a "L1" before any number, then the chemical was NOT DETECTED in the sample.

"Pl." - Present, but less than the level indicated.

Appendix 2.

Summary of Inorganic Acid Data (Sorbent Tubes) from Outdoor Air Samples Collected at Locations Surrounding the World Trade Center, October 30 and 31, 2001

All results are in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$)

Date	Time/Loc.	Site	HCl	H ₃ PO ₄	HNO ₃	H ₂ SO ₄	HBr	HF
10/30/01	PM/RF	140 Broadway	PL10	ND	ND	PL10	ND	15
10/30/01	PM/RF	140 Broadway	PL10	ND	ND	PL10	ND	PL10
10/30/01	PM/ST	140 Broadway	ND	ND	PL10	PL10	ND	ND
10/30/01	PM/ST	140 Broadway	ND	ND	PL10	10	ND	20
10/31/01	AM/RF	140 Broadway	ND	ND	ND	PL10	ND	ND
10/31/01	AM/RF	140 Broadway	PL10	ND	ND	PL10	ND	11
10/31/01	AM/ST	140 Broadway	ND	ND	ND	PL10	ND	11
10/31/01	AM/ST	140 Broadway	PL10	ND	ND	PL10	ND	ND
10/30/01	PM/RF	75 Park Place	ND	ND	ND	PL10	ND	14
10/30/01	PM/RF	75 Park Place	11	ND	ND	ND	ND	11
10/30/01	PM/ST	75 Park Place	ND	ND	PL10	PL10	ND	11
10/30/01	PM/ST	75 Park Place	ND	ND	ND	PL10	ND	12
10/31/01	AM/RF	75 Park Place	VOID	VOID	VOID	VOID	VOID	VOID
10/31/01	AM/RF	75 Park Place	VOID	VOID	VOID	VOID	VOID	VOID
10/31/01	AM/ST	75 Park Place	ND	ND	ND	ND	ND	19
10/31/01	AM/ST	75 Park Place	PL10	ND	ND	PL10	ND	21
10/30/01	PM/RF	225 Rector Place	ND	ND	PL10	15	ND	10
10/30/01	PM/RF	225 Rector Place	PL10	ND	PL10	19	ND	15
10/30/01	PM/ST	225 Rector Place	ND	ND	ND	14	ND	ND
10/30/01	PM/ST	225 Rector Place	ND	ND	PL10	12	ND	11
10/31/01	AM/RF	225 Rector Place	11	ND	PL10	14	ND	ND
10/31/01	AM/RF	225 Rector Place	15	16	PL10	14	ND	ND
10/31/01	AM/ST	225 Rector Place	PL10	ND	PL10	10	ND	13
10/31/01	AM/ST	225 Rector Place	PL10	ND	ND	10	ND	10
10/30/01	PM/RF	Stuyvesant HS	ND	ND	ND	ND	ND	ND
10/30/01	PM/RF	Stuyvesant HS	PL10	ND	ND	ND	ND	PL10
10/30/01	PM/ST	Stuyvesant HS	ND	ND	ND	ND	ND	PL10
10/30/01	PM/ST	Stuyvesant HS	PL10	ND	ND	PL10	ND	ND
10/31/01	AM/RF	Stuyvesant HS	PL10	ND	ND	ND	ND	13
10/31/01	AM/RF	Stuyvesant HS	PL10	ND	ND	ND	ND	17
10/31/01	AM/ST	Stuyvesant HS	ND	ND	ND	ND	ND	10
10/31/01	AM/ST	Stuyvesant HS	ND	ND	ND	PL10	ND	12

- Samples collected and analyzed according to NIOSH Method 7903

- Non-detects and samples with high background concentrations are shown as "ND"

- Samples with concentrations found below the method's applicability are shown as "PL10"

Appendix 3.

Summary of Annular Denuder Tube Extracts from Outdoor Air Samples Collected at the World Trade Center and Surrounding Areas October 30 and 31, 2001

Sample Date	Sampling Location	NH ₄ ⁺ mg / L	NH ₃ ug /m ³	Cl ⁻ mg / L	HCl ug /m ³	NO ₂ ⁻ mg / L	HNO ₂ ug /m ³	NO ₃ ⁻ mg / L	HNO ₃ ug /m ³	SO ₄ ⁼ mg / L	SO ₂ ug /m ³
10/30-31/01	Field Blank	0.44	blank	0.31	blank	0.028	blank	0.038	blank	0.27	blank
10/30-31/01	Field Blank	0.44	blank	0.31	blank	0.00	blank	0.028	blank	0.24	blank
10/30-31/01	Field Blank	0.52	blank	0.31	blank	0.00	blank	0.028	blank	0.43	blank
10/31/01	WTC Debris Pile	39.03	713.9	1.93	33.295	0.033	2.14	0.141	12.408	4.52	59.136
10/31/01	WTC Debris Pile*	39.16	716.3	1.99	34.507	0.036	2.34	0.138	12.142	4.46	58.261
10/30-31/01	225 Rector Place	15.44	27.343	0.73	0.896	0.024	0.16	0.128	1.115	23.14	29.850
10/30/01	225 Rector Place	4.47	20.319	0.31	0.187	0.069	1.24	0.048	1.151	13.02	46.683
10/31/01	225 Rector Place	8.39	41.327	0.52	1.378	0.043	0.80	0.088	2.187	12.79	47.123
10/30-31/01	Stuyvesant HS	3.75	3.628	0.35	0.083	0.026	0.10	0.057	0.300	20.49	15.996
10/30/01	Stuyvesant HS	1.99	4.891	0.45	0.607	0.035	0.39	0.055	0.845	4.45	10.104
10/31/01	Stuyvesant HS	2.81	5.597	0.35	0.186	0.058	0.49	0.087	0.996	15.50	26.152
10/30/01	75 Park Place	1.51	5.692	0.43	0.883	0.00	0.00	0.069	1.787	3.39	13.056
10/30-31/01	75 Park Place	4.11	3.302	0.39	0.113	0.00	0.00	0.068	0.294	25.57	16.372
10/31/01	75 Park Place	2.59	15.984	0.43	1.229	0.050	1.33	0.102	3.661	9.44	50.180

- Samples taken on the roof at Rector and Stuyvesant; sample for Park Place was taken on a 10th floor balcony
- Only one sample was taken at the debris pile; the results shown are from a duplicate analysis.
- Ammonia values were determined from extracts of tubes coated with citric acid.
- Acid gases values were determined from extracts of tubes coated with sodium carbonate.
- Sulfur dioxide values were determined from an oxidized aliquot of the acid gas extracts.

Appendix 4.

Summary of the Aldehyde Results from Outdoor Air Samples

Collected at the World Trade Center and Surrounding Areas, October 30 and 31, 2001

All results are in micrograms per cubic meter ($\mu\text{g}/\text{m}^3$)

Analyte	Detection Limit	140 Broadway				75 Park Place				225 Rector Place				Stuyvesant HS			
		10/30/01		10/31/01		10/30/01		10/31/01		10/30/01		10/31/01		10/30/01		10/31/01	
		Roof	Street	Roof	Street	Roof	Street	Roof	Street	Roof	Street	Roof	Street	Roof	Street	Roof	Street
formaldehyde	1.0	pm	4.4	am	6.6	pm	2.8	pm	3.3	am	7.1	pm	1.5	pm	3.2	pm	am
acetaldehyde	1.0	1.0	1.1	19.7	2.1	13.8	14.4	5.5	3.1	ND	ND	ND	ND	ND	1.4	1.7	1.6
acrolein	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
acetone	1.0	35.6	19.6	ND	13.7	17.4	18.0	12.4	20.5	P	17.3	26.5	24.5	9.4	7.6	9.4	11.9
propionaldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
crotonaldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
butyraldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
benzaldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
isovaleraldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
valeraldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
o-tolualdehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
m-tolualdehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
p-tolualdehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
hexaldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
2,5-dimethylbenzaldehyde	1.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

- Samples collected and analyzed according to EPA Method TO-11

- ND: The analyte was not detected

- P: The analyte was present, but not quantifiable

Appendix 5.
Select VOCs Detected at Debris Pile on 10/31/01*
as Found at Other Sampling Locations

